



AMENDMENTS TO THE SPECIFICATION

Please replace the paragraph on page 1, lines 5-27, with the following amended paragraph:

The present invention relates to a solid catalyst component for ethylene polymerization and copolymerization, composed of a carrier of particulate silica and a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table. The process for producing obtaining the catalyst of the present invention comprises the steps of:

- (a) impregnating an activated silica in particles using with a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
- (b) removing the supernatant liquid from the step (a);
- (c) preparing a solution obtained by reacting at least one magnesium compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
- (d) impregnating the silica obtained in on (b) using the solution prepared in (c);
- (e) optionally reacting the solid obtained in (d) with a reducing agent;
- (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
- (g) thermally treating thermally the solid obtained in (f);
- (h) washing the solid obtained in (g) with an inert organic solvent;
- (i) optionally, washing the solid obtained in (h) with a solution of one or more organometallic compounds of the groups 1, 2, 12 or 13 of the periodic table.

Please replace the paragraphs on page 2, lines 3-30, with the following amended paragraphs:

The slurry or gas phase processes for the production of HDPE or LLDPE operating with low bulk density polymers require polymer need reactors with large volumes in order to obtain the necessary residence time. Particularly, in the gas phase reactors, the presence of fines with low bulk density causes problems troubles. In fact, due to the friction of the polymer particles present in the reactor, into the reactor the fines are especially prone to the formation of electrostatic charges and tend to deposit and adhere to the metallic walls. These stagnant deposits do does not allow the exchange of the reaction heat and become hot spots, which can form layers layer of agglomerates containing eventually melt polymer. After a period of some time chunks of agglomerates can fall down and plug the product discharge system. The described effects are enhanced when the reaction is carried out with a highly active catalyst.

In the U.S. Pat. No. 5,410,002 5.410.002 a summary of patents on the above described phenomena is presented.

Therefore, it is crucial for the process that the catalyst used enables a total control of the polymer morphology resulting in product grains without fines, with high bulk density and good flowing properties.

Another very important aspect is that the catalyst must have a slow decaying time to permit the use of reactors in series. This arrangement makes possible the obtainment of bimodal products in addition to the reduction of the total volume of the reaction for the same production basis. Moreover, process operations operation with a different condition of reaction in at least two reactors in series, makes turns possible the use of catalysts with higher particle size thereby minimizing the formation of electrostatic charges.

2) Polymer Structure

The catalyst properties are fundamental to the polymer structure, mainly with respect ~~of to~~ the molecular weight distribution, comonomer insertion in the polymeric chain and soluble content.

Please replace the paragraphs on page 3, lines 4-27, with the following amended paragraphs:

To obtain a film with improved optical and mechanical properties and avoid blocking problems, a polymer having a narrow molecular weight distribution (MFR < 27), is required. A large quantity of LLDPE applications requires products with a density = 0.918 and a MI = 0.7, and in most cases a xylene soluble content < 10% is desired. Indeed, when the xylene soluble content of the polymer is present in a high concentration (> 10%) and with a low molecular weight, this soluble content tends to migrate to the film surface causing blocking, in addition to the unsatisfactory optical properties (low gloss and high haze).

3) Ziegler-Natta polyethylene catalyst

Due to the strong competition existent in the polyethylene market, the catalyst production cost is a fundamental component. Therefore it is mandatory that the catalyst for producing polyethylene be manufactured by a simple route, from low cost raw material, without generating gaseous, liquid or solid effluents which are hard to treat.

U.S. The Patent US 5,188,997 5.188.997 describes a synthesis process for Ziegler-Natta catalysts from silica and magnesium chloride alcoholate. The results reported demonstrate that this catalyst produces a polymer with low bulk density (0.23 to 0.30 g/ml) and with an intermediate molecular weight distribution (MFR 30.0 to 37.8).

U.S. The Patent US 5,585,317 5.585.317 describes the synthesis of a catalyst supported on a magnesium chloride based carrier. The reported examples relates to the production of

polymers having good morphology, characterized by the absence of fines and by the high bulk density which is, for LLDPE, produced between 0.32 and 0.40 g/ml and for HDPE, between 0.33 and 0.438 g/ml.

Please replace the paragraphs on page 4, lines 4-31, with the following amended paragraphs:

The present invention relates to a solid catalyst component for ethylene polymerization and copolymerization, composed of a carrier of particulate silica and a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table. The process for producing obtaining the catalyst of the present invention comprises the steps of:

- (a) impregnating ~~an~~ activated silica ~~in~~ particles ~~using~~ with a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
- (b) removing the supernatant liquid from the step (a);
- (c) preparing a solution obtained by reacting at least one magnesium compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
- (d) impregnating the silica obtained in ~~on~~ (b) using the solution prepared in (c);
- (e) optionally reacting the solid obtained in (d) with a reducing agent;
- (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
- (g) thermally treating ~~thermally~~ the solid obtained in (f);
- (h) washing the solid obtained in (g) with an inert organic solvent;

(i) optionally, washing the solid obtained in (h) with a solution of one or more metal-alkyl halide compounds of the groups 1, 2, 12 or 13 of the periodic table.

Therefore, the present invention provides a catalyst especially suitable for the production of ethylene homo- and copolymers with a as narrow molecular weight distribution, high density polyethylene (NMWHDPE) and a linear low density polyethylene (LLDPE) with controlled morphology and improved structure.

Please replace the paragraphs beginning on page 5, line 1 to page 8, line 18, with the following amended paragraphs:

Additionally, the catalyst described and claimed in the present invention produces a NMWHDPE with a melt flow ratio (MFR) lower than 27 that is are particularly suitable for thermoforming and injection applications.

Further, the catalyst described and claimed in the present invention produces a LLDPE with a low xylene soluble content due to the very good comonomer insertion allowing the production of films with superior optical properties and very low blocking.

The present invention further defines provides still a catalyst that provides, when submitted to polymerization conditions, particles of polyethylene ethylene homo and ethylene copolymers having a high bulk density and containing a very small quantity of fines.

The present invention provides additionally provides a catalyst useful in liquid phase or in gas phase, ethylene polymerization processes. process.

The present invention further provides further a catalyst useful in polymerization processes process due to its high activity and low decay kinetics.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

FIGURE 1 ~~attached herein~~ is a flowchart, which illustrates the preferred embodiment of the present invention for preparing the solid catalyst ~~component~~ component; and

FIGURE 2 ~~attached herein~~ is a flow diagram of a fluidized bed, gas phase pilot plant used to produce polyethylene.

DETAILED DESCRIPTION

In the present specification, the expression Catalyst Decay means the half-life time of the active sites of a solid catalyst component which is measured as the time required for reaching 50% of the initial catalyst activity during a polymerization run. A catalyst with low decay kinetics has a half-life time preferably higher than 3 hours.

The present invention discloses a solid component obtained from the interaction of a reaction product between at least one magnesium compound, chosen from magnesium halides and magnesium alkoxides and at least one titanium compound chosen from titanium alkoxides and titanium halogen alkoxides, an activated silica impregnated with the organometallic compounds of the groups 1, 2, 12 or 13 and a halogenating agent, capable of interacting with the organometallic compounds of the groups 1, 2, 12 or 13, to give a solid catalyst component, which is highly active in the polymerization and copolymerization of ethylene. Optionally, a reducing agent can be used during the process of preparing preparation of the present catalyst component.

Accordingly, the present invention concerns a process for the preparation of a solid catalyst component ~~of catalyst~~ for the polymerization of ethylene and the copolymerization of

ethylene with alpha-olefins which comprises composed of a carrier of silica in particles (65 to 85 % by weight) and a catalytically active portion (15 to 35 % by weight) including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table. According to FIGURE 1, this process comprises the following steps:

- (a) impregnating an activated silica in particles using with a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
- (b) removing the supernatant liquid from the step (a);
- (c) preparing a solution obtained by reacting at least one magnesium compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
- (d) impregnating the silica obtained in on (b) using the solution prepared in (c);
- (e) optionally reacting the solid obtained in (d) with a reducing agent;
- (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
- (g) thermally treating thermally the solid obtained in (f);
- (h) washing the solid obtained in (g) with an inert organic solvent;
- (i) optionally, washing the solid obtained in (h) with a solution of one or more organometallic compounds of the groups 1, 2, 12 or 13 of the periodic table.

In step (a) of the process according to the present invention, the preferable silica for this purpose is a microspheroidal, porous silica having an average particle size ranging from 10 to 120 mm, preferably between 15 and 100 mm, a SiO₂ contents of > 90% by weight, a surface

area ranging from 250 to 500 m²/g, preferably between 300 and 400 m²/g, a pore volume ranging from 1.0 to 2.0 ml/g, preferably between 1.5 and 1.8 ml/g, and an average pore diameter ranging from 10 to 40 nm, preferably between 20 and 30 nm. This silica should be submitted to an activation treatment before being impregnated, which can be carried out by heating the silica in an inert atmosphere, at a temperature ranging from 100 to 750°C, over a period from 1 to 20 hours. The amount of remaining remained OH on the silica surface after this treatment ranges from 0.1 to 2 mmoles OH per g of silica, preferably between 0.5 and 1.5 mmoles OH per g of silica.

The impregnation is preferably carried out by suspending 10 to 20 parts by weight of silica for each 100 parts by volume of a solution of an organometallic compound of the groups 1, 2, 12 or 13, in aliphatic hydrocarbons, and maintaining the solution with maintained under stirring at a temperature which ranges from room temperature to the boiling point of the solution of the organometallic compound of the groups 1, 2, 12 or 13, in aliphatic hydrocarbons, preferably at room temperature, over a period from 30 to 120 minutes, preferably between 50 and 60 minutes.

The organometallic compounds of groups 1, 2, 12 or 13 of the periodic table suitable for use in the step (a) are alkyl compounds and alkyl halide compounds of metals belonging to these groups, and preferably aluminum, magnesium, lithium and zinc compounds. Specific examples of these compounds are trimethylaluminum, triethylaluminum (TEAL), methylaluminum dichloride, methylaluminum sesquichloride, isobutylaluminum dichloride, isobutylaluminum sesquichloride, ethylaluminum dichloride (EADC), diethylaluminum chloride (DEAC), ethylaluminum sesquichloride (EASC), tri-n-hexylaluminum (Tn-HAL), tri-n-octylaluminum (TnOAL), butyl ethylmagnesium (BEM), butyl octylmagnesium (BOMAG), methylmagnesium chloride and ethylmagnesium chloride. They can be used concentrated or preferably dissolved in the above organic solvent or in a different organic solvent chosen from aliphatic hydrocarbons.

Specific aliphatic hydrocarbons used as solvents for the above mentioned solution can have between 4 and 50 carbons, preferably between 6 and 20 carbons. Specific examples of these

aliphatic hydrocarbons used as solvents are hexane, heptane, octane, isoparaffin, and ~~the most~~
more preferably ~~are~~ hexane and heptane.

In step (a) of the process, the impregnation step using the solution of organometallic ~~compound~~ compounds of the groups 1, 2, 12 or 13, in aliphatic hydrocarbons, is carried out by using an amount of organometallic compound, ranging from 0.1 to 1 mmole of the organometallic solution per mmole of OH on the silica surface, preferably 0.3 to 0.7 mmoles of the organometallic solution per mmole of OH on the silica surface.

At the end of the impregnation treatment, the silica can be removed (step b) ~~(b)~~ from the suspension by usual methods such as settling and siphoning, filtration or centrifugation. The operating temperature of this step can vary from room temperature to the boiling point of the aliphatic hydrocarbon used as the solvent, preferably at room temperature. The wet silica is directly used in the next step.

Please replace the paragraph beginning on page 9, line 27 to page 10, line 7, with the following amended paragraph:

In step (d) the silica obtained in step (b) is suspended in an inert organic solvent, such as a hydrocarbon solvent of the aliphatic type, preferably the same used in the previous steps and the dissolved product prepared in step (c) is added to the suspension. The impregnation is carried out by suspending 100 parts by weight of silica, obtained ~~on~~ in step (b), for each 5 to 200 parts by volume of the component prepared ~~on~~ in step (c) and after dilution in the inert organic solvent. The suspension is maintained under stirring at a temperature that ranges from room temperature to the boiling point of the mixture, preferably at 60°C, over a period of time from 30 to 180 minutes, preferably between 50 and 60 minutes. In this way a solid component suspended in an inert organic solvent is obtained.